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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>5</sup> :</b> <b>C01B 33/18</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 90/10596</b> <b>(43) International Publication Date:</b> 20 September 1990 (20.09.90)
<b>(21) International Application Number:</b> PCT/GB90/00384 <b>(22) International Filing Date:</b> 14 March 1990 (14.03.90)  <b>(30) Priority data:</b> 8905966.1 15 March 1989 (15.03.89) GB  <b>(71) Applicant (for all designated States except US):</b> TSL GROUP PLC [GB/GB]; P.O. Box 6, Wallsend, Tyne and Wear NE28 6DG (GB).  <b>(71)(72) Applicant and Inventor (for all designated States except US):</b> WELLS, Peter, John [GB/GB]; 167 Aycliffe Crescent, Gateshead, Tyne and Wear NE9 7DH (GB).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> SAYCE, Ian, George [GB/GB]; 21 Crabtree Road, Stocksfield, Northumberland NE43 7NX (GB). SMITHSON, Alan [GB/GB]; 12 Pevensey Close, Preston Grange, North Shields, Tyne and Wear NE29 9HW (GB).		<b>(74) Agent:</b> NEWBY, John, Ross; J.Y. & G.W. Johnson, Furnival House, 14-18 High Holborn, London WC1V 6DE (GB).  <b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB, GB (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> IMPROVED VITREOUS SILICA PRODUCTS  <b>(57) Abstract</b>  A process for the manufacture of a synthetic silica product by vapour-phase oxidation of a silica precursor material in a flame not less than 60 % of the silica in the deposited product being derived by oxidation of: (A) one or more straight chain volatile silicon compounds of the general formula: $R_3Si.O(SiR_2O)_n.SiR_3$ and/or (B) one or more cyclic volatile silicon compounds of the general formula: $Si_nO_n(R)_{2n}$ . Doped or undoped fume powder, porous silica soot or fully densified bodies made by the process are also claimed.		

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IMPROVED VITREOUS SILICA PRODUCTSTechnical Field

The present invention relates to the formation of a pure or doped synthetic vitreous silica product by the vapour phase reaction of a volatile compound of silicon. The final product may be in the form of a fume, a porous body of sintered silica soot, or a fully densified body made from vitreous silica. In some applications, the silica may be deposited on a substrate, which may itself be made from silica. The deposited silica may be doped with other elements during or after deposition.

The use of volatile silicon compounds in this type of process is well known. US-A-4038370 discloses that silane ( $\text{SiH}_4$ ) may be oxidised to silica fume, and the fume may be deposited on a substrate to yield a vitreous silica product.

Silane is however expensive, and dangerously pyrophoric. It is thus more common to use a halide as volatile feedstock, and the use of silicon tetrachloride is now widespread throughout the fibre optic and vitreous silica industries. Silicon tetrachloride may thus be oxidised, e.g. in a thermal plasma to give silica fume, and this fume may be deposited on a substrate to give pure vitreous silica containing a low level of hydroxyl (OH), as is described in our GB-A-1061042. The reaction proceeds as follows:



This reaction is exploited commercially in the manufacture of the "water-free" synthetic vitreous silica sold by us under the Registered Trade Mark "WF Spectrosil", which typically contains less than 2 ppm of OH.

As an alternative, silicon tetrachloride may be fed

into an oxyhydrogen flame. Under these circumstances, the reaction is described as flame-hydrolysis, i.e.



The silica may be generated as a fume which can be collected as a porous soot body to be sintered to a pore-free vitreous product in a later process and this is described in US-A-2272342, US-A-3806570 and US-A-4224046. Alternatively the fume may be deposited at such a temperature that it sinters directly to a pore-free vitreous product. In this case the vitreous product is normally found to have a higher level of hydroxyl, but otherwise exhibits very high purity. This is the basis of the manufacture of the optical quality synthetic vitreous silica sold by us under the Registered Trade Mark "Spectrosil" which typically contains about 1000 ppm of OH.

When a low OH content is sought from a product of flame hydrolysis, it is common practice to collect the silica fume as a porous soot body, and subsequently to heat that body in a dehydrating atmosphere containing, e.g. chlorine, or thionyl chloride, before sintering for example in a helium atmosphere, to achieve a pore-free vitreous product. This is the basis of the OVD (Outside Vapour Deposition) and VAD (Vapour-phase Axial Deposition) processes widely used for the manufacture of preforms for optical fibres.

It is desirable in these processes to achieve a large particle fume and thus to manufacture a high density soot with large pore size. The use of silicon tetrachloride as feedstock yields silica fume particles whose size depends on the concentration of vapour species, upon flame temperature and upon the retention time, i.e. the time that the growing particles spend in the flame of the synthesis torch. A conventional co-annular torch, as used in the VAD process will give silica particles typically around 0.08

microns in diameter. H. Suda et al (Proc. 10th Euro. Conf. Opt. Comm. (E.C.O.C.) Sept, 3-6, 1984, Stuttgart, p. 296/7, 1984) - describe how the typical particle size of the fume product can be increased to 0.21 microns by using a "double flame" torch. This torch effectively increases the length of the flame and thereby the retention time of the silica particles. The process of growth of the particles in the flame is thought to be by Brownian collision, followed by coalescence. The longer the particles reside in the flame, the greater the probability of collision between the particles and the larger they become. Coalescence proceeds so long as the temperature remains high enough for such a process, and thereafter the aggregated micro-particles merely form an open chain structure. It is thus advantageous to use a highly exothermic feedstock as this helps to maintain a high flame temperature and thus to promote growth of the particles for a prolonged period.

One of the major drawbacks of using silicon tetrachloride, or any chlorine-containing silicon compound as a precursor for the manufacture of synthetic silica, is the release of chlorine during oxidation, or hydrogen chloride during hydrolysis as a by-product. Both these chemicals are poisonous and corrosive, and any process using silicon tetrachloride, or other chlorosilane compounds, requires extensive gas-extraction and -scrubbing facilities to make it environmentally acceptable.

Despite the difficulties and cost of such scrubbing processes, silicon tetrachloride and certain other chlorosilanes are almost universally used as feedstocks to the above-mentioned processes for the manufacture of silica fume and synthetic vitreous silica. The use of silane ( $\text{SiH}_4$ ) is unusual, costly and hazardous. There is limited mention of the use of alternative silicon compounds, but methyl and ethyl orthosilicates have been proposed for the manufacture of silica powders in DE-A-3500080 and for the manufacture of vitreous products in Japanese unexamined

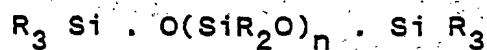
application 85 108338.

The almost universal use of chlorine-containing feedstocks is the more remarkable in that it is impossible thereby to achieve a silica product which is free from contamination by chlorine, which is for some purposes an undesirable impurity.

### Summary of the Invention

The present invention relates to a process for the manufacture of a synthetic silica product by vapour-phase oxidation of a silica precursor material in a flame and collection of the silica from the flow of combustion products by deposition as at least one of a fume powder, a porous silica soot and a fully densified body, characterised in that not less than 60% of the silica in the deposited product is derived by oxidation of

(A) One or more straight chain volatile silicon compounds of the general formula

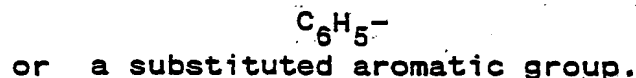


where n is any integer including zero, and R is one or more of the following:

(i) one or more alkyl group(s) of the general formula



(ii) one or more aromatic phenyl group(s)

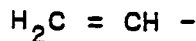


(iii) the hydroxyl group



(iv) the vinyl group

5



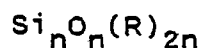
and

(v) the hydride group



5 and/or of

(B) one or more cyclic volatile silicon compounds of the general formula

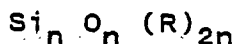


10 where n is an integer greater than 2, and R is one or more of the chemical groups defined at (i) to (v) above,

or a mixture thereof.

More than one type of substituent group may be present in the same molecule.

15 Cyclic molecules covered by the invention have the general formula



where n is greater than 2, preferably greater than 3, and R is a substituent group as defined above or a mixture of such groups.

20 The invention includes the use of mixtures of straight chain molecules as defined above, mixtures of such cyclic molecules, and mixtures of straight chain and cyclic molecules, and also feedstocks containing other species, but of which not less than 60% of the contained oxidisable silicon  
25 species arise from the above-defined molecules.

As noted above, the final size of the particles of silica fume is determined by both nucleation and growth processes. It is preferable for the achievement of large

particles that the molecular weight of the vaporised silica precursor be high, and it is a peculiar advantage of the preferred precursor compounds of the invention that the basic skeleton of vitreous silica is already in place, and the species already contain the polymeric  $(\text{SiO})_n$  chain or ring structure. It is thus possible to achieve a smaller number of primary nuclei, and a larger mean size for the ultimate fume particles.

Excessive carbon is undesirable in combustion reactions to achieve pure silica, since, if combustion is not complete, carbon or silicon carbide may be formed. For this reason, the preferred alkyl group is the methyl group  $\text{CH}_3$ . For the same reason, higher molecular weight silicone species and cyclic molecules may be preferred as these also contain a lower proportion of carbon atoms. Of course, availability, cost, and purity are other factors which may affect the choice of preferred species.

It is a feature of all precursor compounds encompassed by the present invention that in the presence of excess oxygen they burn to form carbon dioxide, water and synthetic silica fume. This fume may be collected on cooling or may be deposited either as pore-free material or as a porous soot on a substrate, which may include any suitably refractory and non-contaminating material, including carbon/graphite, alumina, or vitreous silica which again may be either a pore-free material, or a porous soot body.

The precursor or feedstock compound(s) may be fed to a suitable synthesis burner, the energy input of which may be supplemented by additional combustible gas, for example hydrogen, or methane, together with sufficient oxygen to effect combustion of the contained species. Unlike the commonly used feedstock, silicon tetrachloride, the feedstock compounds of this invention themselves exhibit a substantial heat of combustion. This permits both enhanced temperatures within the reacting core of the burner, and



higher concentrations of Si/O vapour species. These are both desirable requirements giving rise, in a suitably designed synthesis burner, to larger fume particles than is possible using silicon tetrachloride as feedstock. For certain applications such large particle, low surface area fume products, are preferable to those achieved by conventional silica fume manufacturers, typically exhibiting BET surface areas of a minimum of 50 m<sup>2</sup>/g, equivalent to a powder composed of silica spheres each of a diameter of 54 nanometres.

It follows from the high heat of combustion of the preferred feedstocks of the invention that, in a suitably designed silica synthesis burner supplied with precursor, oxidant (for example oxygen), and supplemental hydrogen or methane, at least a third and preferably more than half of the combustion energy of the synthesis flame may be derived from combustion of the precursor. Indeed it is possible to design synthesis burners in which substantially all (e.g. 90% or more) of the combustion energy of the burner is provided by combustion of the precursor compound and these novel features of the synthesis of silica represent further aspects of this invention.

The plume of silica fume derived from the synthesis burner may be cooled and collected as a fume powder using a cyclone, a bag filter or similar equipment. The absence of corrosive gases (e.g. HCl, Cl<sub>2</sub>) in the hot vapours renders this process much simpler, and cheaper, than when silica fume is derived from a chlorine-containing feedstock. Further, it is easier to avoid corrosion-induced contamination.

Alternatively, the plume of silica fume may be projected on to a substrate as described above. The collection efficiency is an important factor in the economics of synthetic silica production, and it is recognised that one of the principal mechanisms of collection of hot fume on a

substrate is the process of thermophoresis, i.e. the tendency of ultra-fine particles in a hot gas stream which exhibits a thermal gradient to be propelled toward the region of lower temperature. It is thus advantageous to  
5 generate the fume in a hot concentrated plume, and project this fume onto a cooler substrate. An important feature of the feedstock compounds included in the present invention is their ability to burn, in a suitably designed synthesis burner, to give a very high temperature plume of silica  
10 fume, gaining maximum benefit from the effect of thermophoresis.

The invention also extends to synthetic silica products made by the process of the invention (e.g. powder material, soot-coated substrates, sintered articles and  
15 fully densified products).

#### Examples of the Invention

The invention will now be further described with reference to the following illustrative Examples:

##### Example 1

20 A heated coannular synthesis burner, comprising a central feed orifice surrounded by a first and second annular channel, was supplied with flows of vapour and gases as follows:

Central orifice: octamethylcyclotetrasiloxane vapour,  
25 0.086 m<sup>3</sup>/h, plus nitrogen, 0.03 m<sup>3</sup>/h.

First annular channel: hydrogen

Second annular channel: oxygen

After ignition, the burner provided a steady flame the central part of which comprised a brightly luminous plume  
30 of silica fume, which was directed on to the side of a

cylindrical graphite substrate of diameter 100 mm, rotating in a glass-working lathe. The burner was mounted on a carriage movable parallel to the axis of the cylindrical graphite substrate, causing the plume of fume progressively and repeatedly to scan the length of the substrate, leading to radial growth on the substrate of an agglomerated white deposit of synthetic silica soot. The burner was withdrawn sufficiently at the end of each pass to maintain a controlled burner-to-substrate distance. The temperature in the deposition zone was maintained at an approximately constant value within the range 1000-1300°C. The deposition was continued for a period of 8 hours.

On cooling and after removal from the graphite substrate, the soot body weighed approximately 5 kg, and had a mean density of  $0.4 \text{ g/cm}^3$ . The body was sintered under vacuum, to give a transparent tube of synthetic vitreous silica glass, of high purity, free from chlorine and with a hydroxyl (OH) content of less than 1 ppm.

#### Example 2

20 A heated coannular synthesis burner, comprising a central feed orifice and four successive annular channels, was supplied with flows of vapour and gases as follows:

Central orifice: decamethylcyclopentasiloxane vapour  
 $0.054 \text{ m}^3/\text{h}$  plus hydrogen,  $0.12 \text{ m}^3/\text{h}$

25 First annular channel: hydrogen

Second annular channel: oxygen

Third annular channel: hydrogen

Fourth annular channel: oxygen.

The axis of the burner was directed at the hemispherical domed end of a cylindrical substrate of vitreous silica, diameter 150 mm, whose surface was maintained at an approximately constant temperature within the range 1500-  
5 1950°C.

A bubble-free agglomerated deposit was thus obtained, comprising a chlorine-free synthetic vitreous silica of high purity and high optical transparency and with a hydroxyl (OH) content of 830 ppm.

### 10 Example 3

A coannular synthesis burner of similar design to that used in Example 1 was supplied with flows of vapour and gases as follows:

Central orifice: octamethylcyclotetrasiloxane vapour,  
15 0.086 m<sup>3</sup>/h, plus aluminium 2,4-pentanedionate vapour, 0.014 m<sup>3</sup>/h, plus nitrogen, 0.03 m<sup>3</sup>/h

First annular channel: hydrogen

Second annular channel: oxygen

20 The flame was directed onto the hemispherical domed end of a cylindrical silica substrate which was rotating about its axis while supported from the other end in a glass-working lathe. A white deposit of alumina-doped silica soot built up on the end of the substrate, which was  
25 continuously withdrawn to maintain a constant burner-to-substrate distance. The temperature of the deposition zone was typically 1140°C.

After a period of 6 hours the deposition was suspended, and the agglomerated soot body was sintered under

vacuum, yielding a body of bubble-free alumina-doped synthetic vitreous silica, with alumina content approximately 1.5 mole%.

#### Example 4

- 5        The conditions of Example 3 were repeated, except that the flows of gas and vapour to the central orifice of the burner were also supplemented by the addition of 0.0052 m<sup>3</sup>/h of titanium tetraisobutoxide vapour. The soot product was thus doped with both alumina and titania, and after  
10        sintering the glass product was found to contain approximately 1.5 mole% alumina and 1.5 mole% titania.

#### Example 5

- 15        The conditions of Example 3 were repeated, except that the flow of aluminium 2,4-pentanedionate was replaced by a flow of 0.0104 m<sup>3</sup>/h of titanium tetraisobutoxide vapour. The soot product was thus singly doped with titania, and after sintering, the glass product was found to contain approximately 3.0 mole% titania.

#### Example 6

- 20        A coannular synthesis burner of similar design to that used in Example 1 was supplied with flows of vapour and gases as follows:

25        Central orifice: octamethylcyclotetrasiloxane vapour, 0.086 m<sup>3</sup>/h plus boron trifluoride diethyletherate vapour, 0.005 m<sup>3</sup>/h plus nitrogen, 0.03 m<sup>3</sup>/h.

First annular channel: hydrogen

Second annular channel: oxygen.

The flame was directed onto the side of a circular cylindrical rod of pure synthetic vitreous silica of diameter 75 mm, rotating in a glass-working lathe. The burner carriage was moved parallel to the axis of the rod causing the plume of doped silica fume progressively and repeatedly to scan the length of the substrate rod, leading to radial growth on the substrate of a white deposit of an agglomerated mass of doped synthetic vitreous silica soot. The temperature in the deposition zone was approximately 1090°C. The deposition was continued for a period of 2 hours.

On cooling, the vitreous silica rod and adhering doped soot layer were subjected to a zone-sintering operation which vitrified the soot leading to a step-index optical fibre preform with a core of pure synthetic vitreous silica and a cladding of synthetic vitreous silica doped with boron and fluorine. The product was drawn to step-index fibre of diameter 200 microns, which had a numerical aperture of 0.16, and an attenuation at 820 nm of 7 dB/km.

#### Example 7

A heated coannular synthesis burner, comprising a central feed orifice surrounded by a first and a second annular channel, was mounted at the lower end of a vertical tube of fused quartz. The burner was supplied with flows of vapour and gases as follows:

Central orifice: octamethylcyclotetrasiloxane vapour, 0.25 m<sup>3</sup>/h, plus nitrogen, 0.10 m<sup>3</sup>/h.

First annular channel: hydrogen

Second annular channel: oxygen

The flame was directed up the tube, at the top of which jets of air were introduced to cool and dilute the flow of

combustion products. The combined gases were led via a water-cooled aluminium tube to a bag-filter. The white silica fume powder which was thus collected was found to have a BET surface area of  $12 \text{ m}^2/\text{g}$ , equivalent to a powder composed of silica spheres each of diameter approximately 220 nanometres.

The following summary demonstrates the use of the present invention.

### Product

- |    |               |   |
|----|---------------|---|
| 10 | Fume          | - collected as large particle/low BET surface area material   |
|    | Soot Body     | - collected on a substrate (which need not be silica)   |
| 15 |               | - collected on a vitreous silica rod, or tube (e.g. on a fibre optic preform).  |
|    |               | - collected on a crucible (inner and/or outer surface)  |
| 20 | Vitreous Body | - collected on a substrate (which need not be silica)   |
|    |               | - collected on a vitreous silica rod, or tube (e.g. on a fibre optic preform).  |
| 25 |               | - collected on a crucible (inner and/or outer surface)  |
|    | Doped Product | - $\text{Al}_2\text{O}_3$ , $\text{GeO}_2$ , $\text{P}_2\text{O}_5$ included as synthetic product is created and/or deposited (for example to raise refractive index) |
| 30 |               | - $\text{B}_2\text{O}_3$ , F included as synthetic product is created and/or deposited (for example to lower  |

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refractive index).

Preferred Feedstocks - Include hexamethyldisiloxane and the straight chain or cyclic tetrameric or pentameric siloxanes. Specifically the siloxanes Octamethylcyclotetra-siloxane and Decamethylcyclopentasiloxane and their mix-  
tures have been found to be especially suitable.

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CLAIMS

1. A process for the manufacture of a synthetic silica product by vapour-phase oxidation of a silica precursor material in a flame and collection of the silica from the  
 5 flow of combustion products by deposition as at least one of a fume powder, a porous silica soot and a fully densified body, characterised in that not less than 60% of the silica in the deposited product is derived by oxidation of

(A) One or more straight chain volatile silicon compounds  
 10 of the general formula



where n is any integer including zero, and R is one or more of the following

(i) one or more alkyl group(s) of the general formula  
 15  $C_m \cdot H_{2m+1}$   
 or a substituted derivative.

(ii) one or more aromatic phenyl group(s)  
 $C_6H_5-$   
 or a substituted aromatic group.

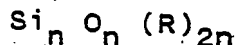
20 (iii) the hydroxyl group  
 $HO -$

(iv) the vinyl group  
 $H_2C = CH -$   
 and

25 (v) the hydride group  
 $H -$

and/or of

B) one or more cyclic volatile silicon compounds of the general formula



where n is an integer greater than 2, and R is one or more  
5 of the chemical groups defined at (i) to (v) above,

or a mixture thereof.

2. A process according to claim 1, characterised in that the vaporised silica precursor material contains a polymeric  $(\text{SiO})_n$  chain and/or ring structure.

10 3. A process as claimed in claim 1 or claim 2, characterised in that at least one half of the energy liberated in the combustion process is derived from combustion of the silica precursor material, and the silica is collected as a porous mass of synthetic silica.

15 4. A process as claimed in claim 1 or claim 2, characterised in that at least one third of the energy liberated in the combustion process is derived from combustion of the silica precursor material, and the silica is collected as a substantially pore-free vitreous product.

20 5. A process as claimed in any preceding claim, characterised in that the silica precursor material is a cyclo-siloxane of the general formula  $\text{Si}_n \text{O}_n (\text{CH}_3)_{2n}$  where n equals 4 or 5.

25 6. A process as claimed in any of claims 2 to 5, characterised in that the silica precursor material is hexamethyldisiloxane.

30 7. A process as claimed in any preceding claim, characterised in that a doping addition is made to the vapour-phase oxidation to modify the properties of the synthetic silica product.

8. A process as claimed in claim 7, characterised in that the doping addition includes the vapour of an oxidisable or hydrolysable compound selected from the group consisting of aluminium, titanium, boron and fluorine.

5 9. A synthetic silica product made by the process of any preceding claim.

10 10. A product according to claim 9, characterised in that the product is an agglomerated mass in the form of one of a cylindrical body, a tubular body, a crucible and an optical fibre preform.

11. A product according to claim 9, characterised in that the product is a fume powder of BET surface area less than  $50 \text{ m}^2/\text{g}$ .

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/00384

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>5</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC5: C 01 B 33/18		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC5	C 01 B; C 03 B; C 03 C	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category	Citation of Document <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	DE, C2, 2909815 (WACKER-CHEMIE GMBH) 22 November 1984, see column 3, line 4  --	1-6
X	DE, A1, 3016010 (DEGUSSA AG) 29 October 1981, see page 5, line 23 - line 34  --	1-6
A	DE, B2, 2313204 (CORNING GLASS WORKS) 8 December 1977, see the whole document  --	1-11
A	DE, A1, 2904199 (DEUTSCHE GOLD- UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER) 7 August 1980, see page 4, line 6 - line 9  --	1-11
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><b>* Special categories of cited documents:</b> <sup>10</sup></p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
1st June 1990	2 6. 06. 90	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	F.W. HECK	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 4113844 (TADASHI TOKIMOTO ET AL) 12 September 1978, see the whole document  -----	1-11

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. PCT/GB 90/00384**

SA 35272

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 07/05/90. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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